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ATOMIC AND MOLECULAR HYDROGEN AND DEUTERIUM:
QUANTUM GASES AND SOLIDS

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ABSTRACT. In the past several years remarkable advances have been made in the experimental conditions under which hydrogen and deuterium can be studied. After the first successful stabilization of atomic gases of spin-polarized hydrogen ($H\uparrow$) and deuterium ($D\uparrow$), a series of experiments were carried out to study their properties. Most challenging has been the attempt to observe Bose Einstein condensation in $H\uparrow$. The access to the required high density has been limited by recombination. Experiments demonstrated that this takes place on the ^4He or ^3He - ^4He surfaces of the cell. Techniques were developed to measure surface adsorption energies and recombination mechanisms. $H\uparrow$ on the helium surface was recognized as an almost ideal 2-dim gas that can also be a superfluid. Recent advances have enabled the polarization of the nuclear as well as the electron spin, suppressing the most important recombination mechanism. This has been directly demonstrated by ESR measurements. Significantly higher densities and thus phenomena of the degenerate quantum gases are promised.

Molecular hydrogen and deuterium form lattices of quantum mechanical free rotors at $T \approx 14$ K and low pressure. Increasing density of the solid distorts this picture. Pressures as high as 600 kbar have been achieved at $T = 1.1$ K. In solid ortho-deuterium a broken rotational symmetry phase transition has been observed at 278 kbar while H_2 maintains its low pressure state to the highest densities yet achieved. At still higher pressures a transition to a metallic phase is expected. Equation of state measurements predict this to be in the 2-6 megabar region.

INTRODUCTION

Atomic hydrogen is the simplest atom in the universe. The role it has played in the development and the formation of the foundations of our understanding of modern physics is far more profound than might be superficially assumed by viewing its lonely position in the periodic table of the elements. Its simplicity offers a naive and sometimes irresistible allure to experimentalist and theorist alike to use this simple atom to unveil nature's deepest secrets. Yet it is humbling when we realize how tightly

these secrets are guarded [1].

In the early seventies, a two-pronged program was started at the University of Amsterdam to study this system and its isotope, deuterium. The most speculative prong had as its quest the investigation and creation of conditions under which a many-body system of the atomic species could be produced. The second prong was to submit solid molecular hydrogen, the simplest molecular solid, to high pressures as a means of probing the dynamics and interactions of this quantum solid. Common denominators of the studies were low temperature, to place the system in or near the ground state, and spectroscopy to study the low-lying spectra of excitations.

STABILIZED GASES OF ATOMIC HYDROGEN AND DEUTERIUM

Atomic hydrogen has been studied since before the twentieth century and played a pivotal role in the development of modern quantum mechanics. However, it could only be produced in high temperature discharges or low density atomic beams. Early on it became clear that a high density of the gas would not easily be achieved. In fact, until a few years ago the consensus was that it was not possible to produce this explosively unstable gas. The reason for this is seen in fig. 1 of the Kolos-Wolniewicz interaction potential of the two ground state $1s$ atoms. The singlet potential, $^1\Sigma_g^+$, with the

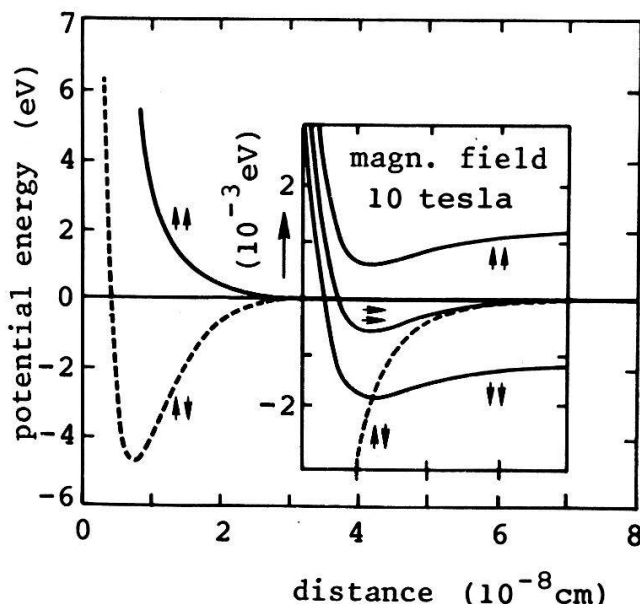


Figure 1

The interaction potentials for hydrogen in the singlet (dashed curve) and triplet state. The inset shows the effect of a magnetic field on an amplified vertical scale.

electron spins aligned antiparallel, possesses a deep attractive well. Two atoms form a molecule with a large dissociation energy, $D/k_B \approx 52000$ K. The probability that two free atoms recombine to form a molecule in a three-body collision is very high. On the other hand, if the electron spins are parallel, the interaction potential, ${}^3\Sigma_u^+$, has a well depth of but 6.46 K and does not support a bound molecular state because of the large zero-point energy. There appears to be no potential barrier between the atomic and molecular states. Even a magnetic field of 10 T has a Zeeman interaction energy with the electronic magnetic moment of only ~ 13 K, which is insignificant with respect to the binding energy. Since a normal gas of hydrogen has a 50-50 up-down spin distribution, collisions of two atoms in the presence of a third body result in rapid formation of the molecular species. At a density of 10^{19} atoms/cm³, the half life of the gas for decay to H₂ is of order 10^{-7} seconds.

Early on we realized [2] that although there was no barrier between the atomic and molecular states, electron spin polarization made recombination a forbidden process. Thus a gas of spin-polarized hydrogen (H \downarrow) in which all of the atoms had pairwise interactions on the ${}^3\Sigma_u^+$ potential might possibly be stable, or at least long-lived at moderately high densities. An experiment was conceived in which a beam of atomic hydrogen would be spin polarized in the spin-up states by passage through a hexapole magnet. The atoms would then be condensed on a cold substrate ($T \approx 1.5$ K) of inert closed shell atoms as a 2-dim gas in a small magnetic field of order 0.2 T, used to define the polarization. The experiment was carried out with a disastrous result [3]. On the inert surface the spins rapidly depolarized and the atoms recombined to form H₂. The lessons learned were that surfaces can be highly destructive of the gas. Furthermore, one should try to stabilize the gas in the ground electronic spin-down state and at lower temperatures in substantially stronger fields so that the spin-down polarized state is overwhelmingly statistically favored.

A new apparatus was constructed with the objective of stabilizing H \downarrow in the spin-down state as a 3-dim gas. A magnetic field of order 10 T was used, and temperatures of order 300 mK were available. This would provide a Boltzmann factor of $\sim 10^{20}$ favoring spin down. The apparatus is shown in fig. 2. Hydrogen, from a microwave discharge, is transported via teflon tubes to the low temperature high field region. The gas is automatically

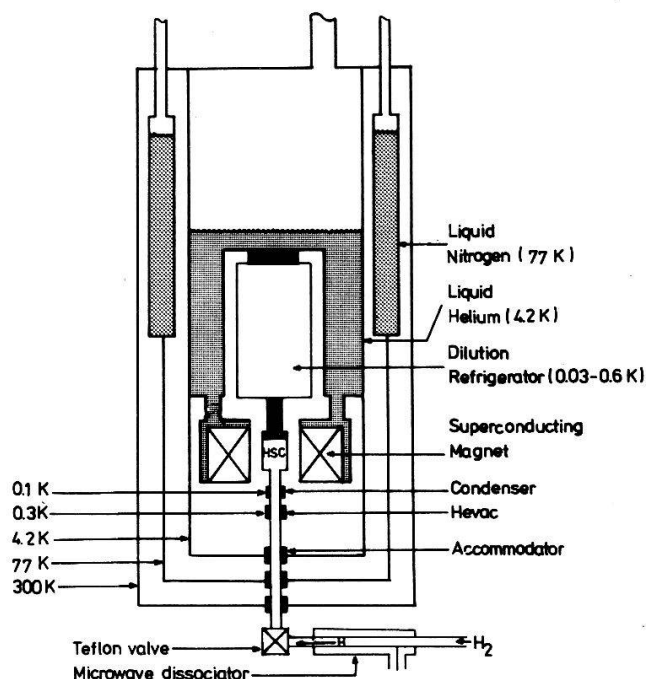


Figure 2

A schematic of an apparatus for studying atomic hydrogen. The HSC is the hydrogen stabilization cell.

polarized and selected by the field gradients as the atoms enter the cell. Condensation and subsequent recombination on surfaces is suppressed by covering all surfaces with a film of superfluid ^4He . Due to the very small adsorption energy, H does not stick to liquid ^4He , except at very low temperatures. $\text{H}\downarrow$ is kept in the cell by the magnetic field gradient which acts as a confining potential. The gas is detected by means of microcalorimetry. A bolometer is heated to desorb the protective helium film which allows the atoms to rapidly condense and recombine, liberating their easily measured recombination energy. A gas with a density of approximately 10^{14} atoms/cm³ was first stabilized for times extrapolated to hours in October, 1979 [4]. Within some months, these results were confirmed by measurements at MIT [5] and Cornell [6] in high fields and by an alternate technique in zero-field at UBC [7].

We proceeded to increase the density by two to three orders of magnitude [8] and established that $\text{H}\downarrow$ was gaseous by measuring the magnetic equation of state. Subsequent measurements down to $T \approx 80$ mK support the idea that $\text{H}\downarrow$ will remain gaseous down to $T = 0$ K.

The quest for higher densities and low temperatures was driven by the desire to observe Bose-Einstein condensation in this gas of Bosons. The

critical temperature is

$$T_c = 3.31 \frac{n^2}{mk_B} (n/g)^{2/3}$$

where n is the density, g the spin degeneracy, and m the mass of $H\downarrow$. This corresponds to $T_c = 100$ mK for a density of $1.6 \times 10^{19}/\text{cm}^3$. The complementary system $D\downarrow$, a gas of fermions, also expected to show spectacular quantum behavior at high densities, was also stabilized [9], but limited to maximum densities of $\sim 10^{14}/\text{cm}^3$. It was shown that recombination took place principally on the ^4He surface. The low density was a result of the large measured adsorption energy, $\epsilon_a/k_B = 2.6$ K, which resulted in large surface densities and rapid recombination. In two theoretical papers [10] it was shown that $H\downarrow$ (or $D\downarrow$) would have a saturation coverage on the He surface of $n_s^{\text{sat}} = \epsilon_a/2V_{\text{int}}$ (V_{int} is the positive interaction energy of a 2-dim gas of $H\downarrow$). This coverage must be achieved before the gas can Bose condense, a stringent requirement, since the recombination rate is proportional to n_s^2 ; this large recombination heating prevents achievement of the required low temperatures. The adsorption energy of H on ^4He was measured at both UBC [11] and Amsterdam [12] and found to be $\epsilon_a/k_B \approx 1$ K. ^3He and $^3\text{He}-^4\text{He}$ surfaces were studied by both these groups and $\epsilon_a/k_B \approx 0.35$ K was found [13]. This implies that higher densities could be achieved with ^3He surfaces, but not sufficiently high to attain BEC.

In Amsterdam it was shown that the principal interaction responsible for recombination was the hyperfine interaction, $a\vec{I} \cdot \vec{S}$ [12]. The ground hyperfine state, $|a\rangle \approx -|\downarrow\uparrow\rangle + \epsilon|\uparrow\uparrow\rangle$ (\uparrow , electron spin projection; \uparrow , nuclear spin projection; $\epsilon = a/2\mu^+B$ where a is the hyperfine coupling constant, μ^+ the electron plus nuclear magnetic moment and B the magnetic field), is an admixed spin state, whereas the other electron spin-down hyperfine state, $|b\rangle = |\downarrow\uparrow\rangle$ is a pure Zeeman state. Pairs of atoms in the a - a or a - b state have a quantum mechanical projection on the molecular state and collisions of these pairs can lead to recombination, whereas b - b collisions cannot, for the dominant hyperfine mechanism. Statt and Berlinsky [14] made the interesting suggestion that the very long nuclear relaxation time T_1 between the $|a\rangle - |b\rangle$ levels should result in a bottlenecking so that a gas of a - b atoms would be preferentially depleted of the $|a\rangle$ -state, leading to a gas of pure $|b\rangle$ -state atoms, i.e., electron and nuclear polarized, or double polarized hydrogen, $H\uparrow\uparrow$. The lifetime of the gas would then be determined by

$2Gn = T_1^{-1}$, the nuclear relaxation rate, which feeds atoms into the reactive $|a\rangle$ -state. An attempt to achieve this state was made in Amsterdam [15], but short nuclear relaxation times were observed. The MIT group succeeded in producing $H\downarrow\uparrow$ with long nuclear T_1 's [16]. The difficulty in the Amsterdam measurements was found to arise from magnetic impurities in the cell walls. A careful construction of a clean, etched cell led to nuclear polarizations as high as 99.8% [17]. Nuclear relaxation rates measured first at MIT and confirmed at Amsterdam were in agreement with theory for volume relaxation, but substantially faster than the theoretical predictions for surface relaxation. High field ESR experiments in Amsterdam [18] were used to directly measure the population of the $|a\rangle$, $|b\rangle$ states as a function of time, as the gas self-polarized.

Since $H\downarrow\uparrow$ has a much lower recombination rate than $H\downarrow$, a gas of $H\downarrow\uparrow$ can possibly be compressed to the densities required for BEC. Recent compression experiments in Amsterdam [19] have obtained densities of $\sim 2 \times 10^{18}/\text{cm}^3$, an increase of an order of magnitude over the previous maximum; however, BEC remains an experimental challenge.

SOLID MOLECULAR HYDROGEN AND DEUTERIUM AT HIGH PRESSURE

At zero pressure, solid molecular H_2 and D_2 possess a number of unique quantum mechanical properties [20]. Due to the weak intermolecular interactions and light masses, these systems are quantum solids, i.e., the molecules have a large zero-point motion relative to the lattice parameters. As a result, translational dynamics are highly anharmonic; the highly compressible lattice is expanded, with a nearest neighbor distance of 3.8 \AA at zero pressure for H_2 . Due to the weak anisotropic interactions, the molecular rotational quantum number J [the energy $E = BJ(J+1)$] remains a good quantum number in the solid. Thus the zero-pressure solid is an assembly of molecules loosely bound to lattice sites, in free-rotor rotational states. Due to the nuclear spin, H_2 (or D_2) has two molecular species, ortho and para; $p\text{-}H_2$ and $o\text{-}D_2$ correspond to the even J -species, while $o\text{-}H_2$ and $p\text{-}D_2$ correspond to the odd J -species. At the low temperature of the solids ($T \lesssim 19 \text{ K}$) only the lowest rotational states are populated. Since conversion from ortho to para is very slow, solids of almost pure $J=0$ or $J=1$ molecules can be prepared and studied.

$p\text{-}H_2$ and $o\text{-}D_2$, in the spherically symmetric $J=0$ state, form hcp

lattices and remain so to $T = 0$ K. Although $J=1$ $o\text{-H}_2$ and $p\text{-D}_2$ form the hcp lattice upon freezing, at temperatures somewhat below 4.2 K they undergo an orientational ordering phase transition to the Pa3 structure.

In Amsterdam a program was started to study the effects of pressure on these solids. Three objectives motivated the work. By compressing a quantum solid, lattice particles are localized and the gradual transition from quantum solid to quasi-harmonic behavior of the dynamical properties (phonons) could be studied. Secondly, the radial dependence of the intermolecular potential was expected to be strong, but had not yet been experimentally probed and compared to a number of current *ab initio* calculations. Third, it was expected that the anisotropic interactions which increase rapidly with density, would result in the admixture of higher rotational states into the ground state. Eventually this should lead to the breakdown of J as a good quantum number, and even the "spherical" $J=0$ solids of zero pressure would enter an orientationally ordered state.

A first series of experiments was carried out to pressures up to about 6 kbar. A number of pressure techniques were developed to enable compressing ortho and para species to these pressures with high quality crystals. Both optical (Raman and far infrared) and equation of state (EOS) measurements were carried out. FIR studies of the phonons showed that the anharmonic behavior resulting in broad one-phonon responses persisted to high pressures. Even though the molecules were increasingly localized, final state relaxation channels were opened up as the pressure increased [21]. Raman techniques were developed which enabled a determination of the single molecule rotational wave function as a function of density [22]. It was found that even at zero pressure a small ($\sim 1\%$) admixture of higher rotational states into the ground $J=0$ or 1 state was present. The EOS of H_2 was determined up to 25 kbar by combining our isochoric measurements up to 2 kbar with a number of measurements from the literature [23].

In the late 1970's we decided to try to probe the very high density regime of H_2 and D_2 and built a diamond anvil cell (DAC) to operate at liquid helium temperatures. With this cell, shown in fig. 3, we have attained pressures as high as 600 kbar.

A number of fascinating phenomena have been observed in $p\text{-H}_2$ and $o\text{-D}_2$. The transverse phonon of the hcp structure, the $J=0 \rightarrow 2$ rotons, and the $v=0 \rightarrow 1$ vibrons can be studied by means of Raman scattering. An interesting

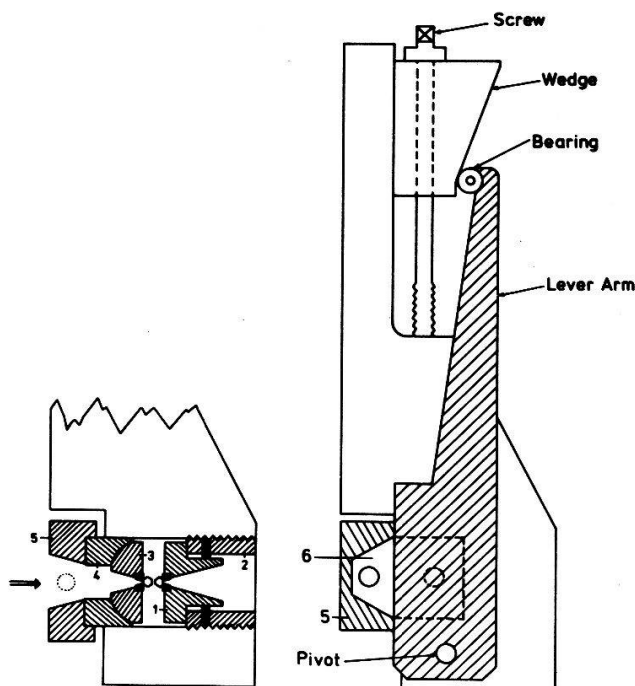


Figure 3

The diamond anvil cell used for high pressure, low temperature studies of H_2 and D_2 .

"text book" example of mode hybridization has been observed. Although the phonon frequency rapidly increases with density, the center of mass of the three distinct roton lines shown in fig. 4 remains almost unshifted. As a result the phonon which should cross the rotons, hybridizes with a roton of the same symmetry.

In 1972 Raich and Etters [24] first predicted that at a high enough density the mixing of the rotational states would result in a spontaneous symmetry breaking and the distorted molecules would go into an orientationally ordered phase. The predicted pressure was ~ 50 kbar. Recently, we have observed this phase transition in $o\text{-}D_2$ at a pressure of 278 kbars [25]. The phase transition was detected by observation of both a change of the rotational Raman spectrum (see fig. 4) and a shift of the vibron frequency.

Our most recent work has been to extend the EOS of H_2 and D_2 at $T = 4.2$ K by about a factor of 20, up to 400 kbar, using our DAC [26]. The EOS requires the measurement of both pressure, P , and molar volume, V . Pressure measurements are straightforward from the calibrated ruby spectrum. The volume has been determined directly by measuring the volume of the cylindrical chamber containing the sample. The area of the hole (diam ≈ 100 microns) was

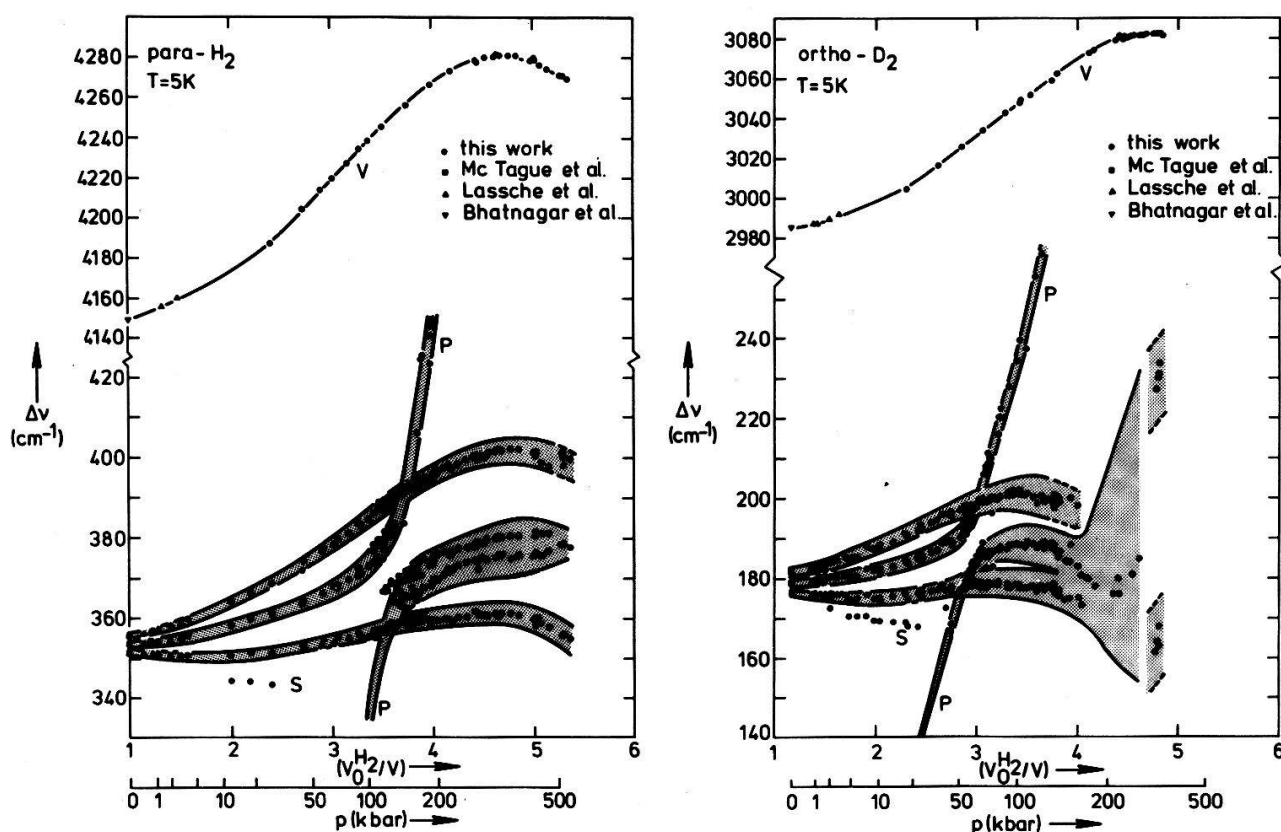


Figure 4

Raman spectra of H_2 and D_2 as a function of pressure or density. P is the phonon, V the vibron. The remaining lines are rotons. S is a spurious, strain induced line. The shading indicates the line width. $V_0^{\text{H}_2}$ is the zero pressure molar volume of H_2 , used as a common scale factor for H_2 and D_2

measured by microphotographic techniques, and the thickness ($d \approx 10\text{--}20$ microns) by optical interference techniques. The resulting EOS is shown in fig. 5, along with an extrapolation to higher densities.

One of the interesting results is that a new prediction can be made for the critical pressure required to transform H_2 to the conducting metallic state. This occurs when the Gibbs free energy of the molecular and metallic phases are equal. In fig. 6 we show the experimentally determined Gibbs energy for the insulating phase, extrapolated to higher density, as well as the theoretical Gibbs energy of the metallic phase. The predicted pressure of 2-6 megabars for the transition will be a great challenge for experimentalists in the 1980's.

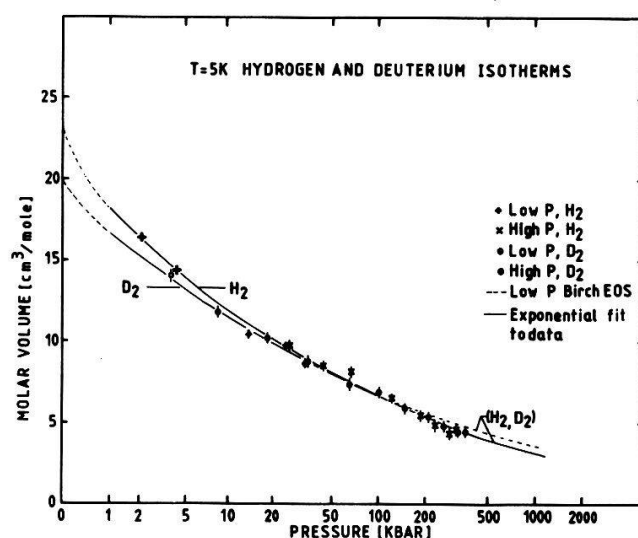


Figure 5

The EOS of H_2 and D_2 obtained with a DAC. The lines are fitted expressions for the EOS which can be extrapolated to high pressure.

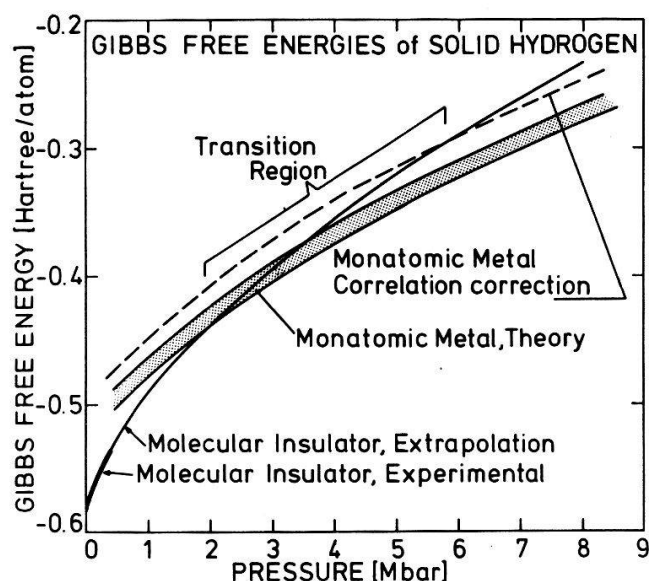


Figure 6

The Gibbs free energy of molecular and atomic hydrogen as a function of pressure. The phase transition occurs at the crossing. A spread in theoretical values for the metallic phase is indicated by shading and the dashed curve.

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